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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C07C 69/734, A01N 37/14, 37/06, 31/14, 31/04 — A1

(11) International Publication Number: WO 96/29301

(43) International Publication Date: 26 September 1996 (26.09.96)

(21) International Application Number: PCT/GB96/00658

(22) International Filing Date: 19 March 1996 (19.03.96)

(30) Priority Data:
9505651.1 21 March 1995 (21.03.95) GB

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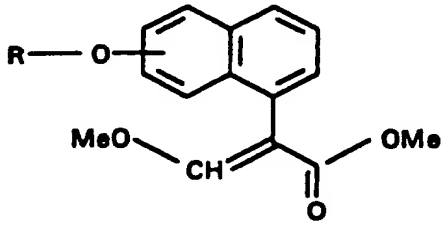
(81) Designated States: AU, BG, BR, CA, CN, CZ, HU, JP, KR, KZ, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TR, UA, US, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: FUNGICIDAL COMPOUNDS

(57) Abstract

Compounds of formula (I), wherein R is alkyl, cycloalkyl, alkenyl cycloalkenyl, alkynyl, phenyl or heterocyclyl, each of which is optionally substituted, or is hydrogen, have pesticidal, especially fungicidal, activity.



(I)

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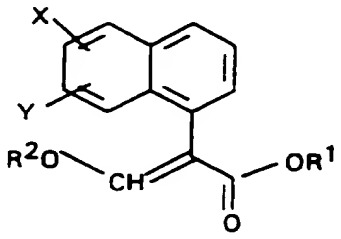
Fungicidal compounds

This invention relates to compounds having pesticidal, especially fungicidal, insecticidal and acaricidal, activity.

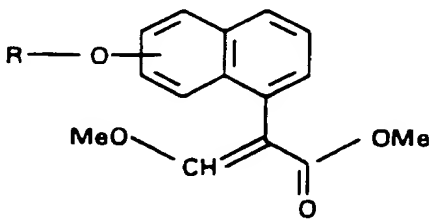
In EP 267734 there are claimed compounds of formula



wherein X and Y, which are the same or different, are hydrogen, halogen, optionally substituted alkyl, optionally substituted cycloalkyl, optionally substituted cycloalkylalkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heteroaryl, optionally substituted alkoxy, optionally substituted aryloxy, optionally substituted heteroaryloxy, optionally substituted arylalkoxy, optionally substituted heteroarylalkoxy, optionally substituted acyloxy, optionally substituted amino, acylamino, nitro cyano, $-CO_2R^3$, $-CONR^4R^5$, or $-COR^6$, except that X and Y are not both hydrogen; R^1 and R^2, which are the same or different, are alkyl or fluoroalkyl; and R^3, R^4, R^5 and R^6, which are the same or different, are hydrogen, alkyl, alkenyl, alkynyl, optionally substituted aryl, optionally substituted aralkyl, or cycloalkylalkyl.

In this specification no compounds are disclosed in which X or Y are radicals attached to the naphthyl group via an oxygen atom. We have now found a certain group of such compounds falling within this claim have particularly valuable pesticidal, especially fungicidal, insecticidal and acaricidal, activity.

The invention provides compounds of formula I



(I)

wherein

R is alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, phenyl or heterocyclyl, each of which is optionally substituted, or is hydrogen, and acid addition salts of any compounds which are basic and basic addition salts of any compounds which are acidic.

The R-O- group is preferably attached to the naphthyl at the 6 or 7 position and more preferably at the 7-position.

Substituents when present on any phenyl or heterocyclyl group include for example halogen, cyano or nitro, or the group $D-(L)_m-$, where m is 0 or 1, L is O, S, SO,.SO_2, CO, O-CO or CO-O, and D is has the same meaning as R (except hydrogen when m is 0) or is optionally substituted amino; or two adjacent groups on the ring together with the atoms to which they are attached can form an carbocyclic or heterocyclic ring which may be similarly substituted as for phenyl.

The term heterocyclyl includes both aromatic and non-aromatic heterocyclyl groups. Heterocyclyl groups are generally 5, 6 or 7-membered rings containing up to 4 hetero atoms selected from nitrogen, oxygen and sulfur. Examples of heterocyclyl groups are furyl, thienyl, pyrrolyl, pyrrolinyl, pyrrolidinyl, imidazolyl, dioxolanyl, oxazolyl, thiazolyl, imidazolyl, imidazolinyl, imidazolidinyl, pyrazolyl, pyrazolinyl, pyrazolidinyl, isoxazolyl, isothiazolyl, oxadiazolyl, triazolyl, thiadiazolyl, pyranyl, pyridyl, piperidinyl, dioxanyl, morpholino, pyridazinyl, pyrimidinyl, pyrazinyl, piperazinyl, triazinyl, thiazolinyl, benzimidazolyl, tetrazolyl, benzoxazolyl, imidazopyridinyl, benzoxazinyl, benzothiazinyl, oxazolopyridinyl, benzofuranyl, quinolinyl, quinazolinyl, quinoxalinyl, sulfolanyl, dihydroquinazolinyl, benzothiazolyl, phthalimido, benzofuranyl, azepinyl, oxazepinyl, thiazepinyl, diazepinyl and benzodiazepinyl. Heterocyclyl groups may themselves be substituted for example as for phenyl.

Alkyl groups are preferably of 1 to 8, e.g. 1 to 6, carbon atoms. Alkenyl and alkynyl groups are generally of 3 to 6 carbon atoms. Cycloalkyl or cycloalkenyl groups are preferably of 3 to 8 carbon atoms.

Substituents, when present on any alkyl, cycloalkyl, cycloalkenyl, alkenyl or alkynyl moiety include halogen, cyano, optionally substituted alkoxy, optionally substituted alkylthio, hydroxy, nitro, optionally substituted amino, acyl, acyloxy, optionally substituted phenyl, optionally substituted heterocyclyl, optionally substituted phenoxy and optionally substituted heterocyclyloxy.

Cycloalkyl or cycloalkenyl groups may also be substituted by alkyl.

Amino groups may be substituted for example by one or two optionally substituted alkyl or acyl groups, or two substituents can form a ring, preferably a 5 to 7-membered ring, which may be substituted and may contain other hetero atoms, for example morpholine, thiomorpholine, or piperidine.

The term acyl includes the residue of sulfur and phosphorus-containing acids as well as carboxylic acids. Examples of acyl groups are thus $-COR^5$, $-COOR^5$, $-CXNR^5R^6$, $-CON(R^5)OR^6$, $-COONR^5R^6$, $-CON(R^5)NR^6R^7$, $-COSR^5$, $-CSSR^5$, $-S(O)_pR^5$, $-S(O)_2OR^5$, $-S(O)_pNR^5R^6$, $-P(=X)(OR^5)(OR^6)$, $-CO-COOR^5$, where R^5, R^6 and R^7 which may be the same or different, are hydrogen, optionally substituted alkyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted phenyl or optionally substituted heterocyclyl or R^6 and R^7 together with the atom(s) to which they are attached can form a ring, p is 1 or 2 and X is O or S.

The compounds of the invention exist as the E and Z isomers and the invention includes individual isomers as well as mixtures of these, with the E-isomer being preferred.

A preferred group of compounds are those where R is alkyl, substituted by one or more alkoxy, aryloxy, heteroaryloxy or heterocyclyoxy groups. (all of which may be optionally substituted). A particularly preferred group of this type $Y-O-(CH_2)_n-$, where Y is optionally substituted aryl, heteroaryl, heterocyclyl and heteroaryl, and n = 1-4, especially 2

Another preferred group of compounds are those where R is optionally substituted heteroaryl, e.g. pyrimidinyl, 1,2,4-thiadiazolyl, quinazolinyl or pyridyl.

A particularly preferred group of compounds are those where R is an optionally substituted C_1-C_6 linear or branched chain alkyl group, preferably substituted by one or more halogen atoms, especially fluorine and/or chlorine and/or bromineatoms. Examples of such preferred groups include CF_2H, CF_2Br, CF_2CF_2Cl, $CFClCF_2Cl$. CF_2CF_2H or CF_2CHCl_2.

The invention includes any compound of formula I and specifically listed.

The compounds of the invention have activity as fungicides, especially against fungal diseases of plants, e.g. mildews and particularly barley powdery mildew (*Erysiphe graminis*) and vine downy mildew (*Plasmopara viticola*), rice blast (*Pyricularia oryzae*), cereal eyespot (*Pseudocercosporella herpotrichoides*), rice sheath blight (*Pellicularia sasakii*), grey mould (*Botrytis cinerea*), damping off (*Rhizoctonia solani*), wheat brown rust (*Puccinia recondita*), late tomato or potato blight (*Phytophthora infestans*), apple scab (*Venturia inaequalis*), glume blotch (*Leptosphaeria nodorum*). Other fungi against which the compounds may be active include other powdery mildews, other rusts, and general pathogens of Deuteromycete, Ascomycete, Phycomycete and Basidomycete origin.

The compounds of the invention also have insecticidal, acaricidal and nematicidal activity and are particularly useful in combating a variety of economically important insects, acarids and plant nematodes, including animal ectoparasites and especially Diptera, such as sheep blow-fly, *Lucilia sericata*, and house-flies, *Musca domestica*; Lepidoptera, including *Plutella xylostella*, *Spodoptera littoralis*, *Heliothis armigera* and *Pieris brassicae*; Homoptera, including aphids such as *Megoura viciae* and *Aphis craccivora*; Coleoptera, including corn rootworms (*Diabrotica* spp., e.g. *Diabrotica undecimpunctata*); and spider mites, such as *Tetranychus* spp..

The invention thus also provides a method of combating pests (i.e. fungi, insects, nematodes, acarids and weeds) at a locus infested or liable to be infested therewith, which comprises applying to the locus a compound of formula I. Some novel compounds of formula I have weak pesticidal activity but still have utility as intermediates and such compounds also form one aspect of the invention.

The invention also provides an agricultural composition comprising a compound of formula I in admixture with an agriculturally acceptable diluent or carrier.

The composition of the invention may of course include more than one compound of the invention.

In addition the composition can comprise one or more additional active ingredients, for example compounds known to possess plant-growth regulant, herbicidal, fungicidal, insecticidal or acaricidal properties. Alternatively the compound of the invention can be used in sequence with the other active ingredient.

The diluent or carrier in the composition of the invention can be a solid or a liquid optionally in association with a surface-active agent, for example a dispersing agent, emulsifying agent or wetting agent. Suitable surface-active agents include anionic compounds such as a carboxylate, for example a metal carboxylate of a long chain fatty acid; an N-acylsarcosinate; mono- or di-esters of phosphoric acid with fatty alcohol ethoxylates or salts of such esters; fatty alcohol sulfates such as sodium dodecyl sulfate, sodium octadecyl sulfate or sodium cetyl sulfate; ethoxylated fatty alcohol sulfates; ethoxylated alkylphenol sulfates; lignin sulfonates; petroleum sulfonates; alkyl-aryl sulfonates such as alkyl-benzene sulfonates or lower alkylnaphthalene sulfonates, e.g. butyl-naphthalene sulfonate; salts of sulfonated naphthalene-formaldehyde condensates; salts of sulfonated phenol-formaldehyde condensates; or more complex sulfonates such as the amide sulfonates, e.g. the sulfonated condensation product of oleic acid and N-methyl taurine or the dialkyl sulfosuccinates, e.g. the sodium sulfonate of dioctyl succinate. Nonionic agents include condensation products of fatty acid esters, fatty alcohols, fatty acid amides or fatty-alkyl- or alkenyl-substituted phenols with

ethylene oxide, fatty esters of polyhydric alcohol ethers, e.g. sorbitan fatty acid esters, condensation products of such esters with ethylene oxide, e.g. polyoxyethylene sorbitan fatty acid esters, block copolymers of ethylene oxide and propylene oxide, acetylenic glycols such as 2,4,7,9-tetramethyl-5-decyne-4,7-diol, or ethoxylated acetylenic glycols.

Examples of a cationic surface-active agent include, for instance, an aliphatic mono-, di-, or polyamine as an acetate, naphthenate or oleate; an oxygen-containing amine such as an amine oxide or polyoxyethylene alkylamine; an amide-linked amine prepared by the condensation of a carboxylic acid with a di- or polyamine; or a quaternary ammonium salt.

The compositions of the invention can take any form known in the art for the formulation of agrochemicals, for example, a solution, a dispersion, an aqueous emulsion, a dusting powder, a seed dressing, a fumigant, a smoke, a dispersible powder, an emulsifiable concentrate or granules. Moreover it can be in a suitable form for direct application or as a concentrate or primary composition which requires dilution with a suitable quantity of water or other diluent before application.

An emulsifiable concentrate comprises a compound of the invention dissolved in a water-immiscible solvent which is formed into an emulsion with water in the presence of an emulsifying agent.

A dusting powder comprises a compound of the invention intimately mixed and ground with a solid pulverulent diluent, for example, kaolin.

A granular solid comprises a compound of the invention associated with similar diluents to those which may be employed in dusting powders, but the mixture is granulated by known methods. Alternatively it comprises the active ingredient absorbed or adsorbed on a pre-granular diluent, for example, Fuller's earth, attapulgite or limestone grit.

Wettable powders, granules or grains usually comprise the active ingredient in admixture with a suitable surfactant and an inert powder diluent such as china clay.

Another suitable concentrate is a flowable suspension concentrate which is formed by grinding the compound with water or other liquid, a wetting agent and a suspending agent.

The concentration of the active ingredient in the composition of the present invention, as applied to plants is preferably within the range of 0.0001 to 1.0 per cent by weight, especially 0.0001 to 0.01 per cent by weight. In a primary composition, the amount of active ingredient can vary widely and can be, for example, from 5 to 95 per cent by weight of the composition.

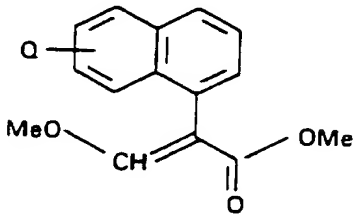
In the method of the invention the compound is generally applied to seeds, plants or their habitat. Thus, the compound can be applied directly to the soil before, at or after drilling so that the presence of active compound in the soil can control the growth of fungi which may attack seeds. When the soil is treated directly the active compound can be applied in any manner which allows it to be intimately mixed with the soil such as by spraying, by broadcasting a solid form of granules, or by applying the active ingredient at the same time as drilling by inserting it in the same drill as the seeds. A suitable application rate is within the range of from 5 to 1000 g per hectare, more preferably from 10 to 500 g per hectare.

Alternatively the active compound can be applied directly to the plant by, for example, spraying or dusting either at the time when the fungus has begun to appear on the plant or before the appearance of fungus as a protective measure. In both such cases the preferred mode of application is by foliar spraying. It is generally important to obtain good control of fungi in the early stages of plant growth as this is the time when the plant can be most severely damaged. The spray or dust can conveniently contain a pre- or post-emergence herbicide if this is thought necessary. Sometimes, it is practicable to treat the roots of a plant before or during planting, for example, by dipping the roots in a suitable liquid or solid composition. When the active compound is applied directly to the plant a

suitable rate of application is from 0.001 to 1 kg per hectare, preferably from 0.05 to 0.5 kg per hectare.

The compounds of the invention may be prepared, in known manner, in a variety of ways, for example

a) by reacting a compound of formula II



(II)

wherein Q is a leaving group, preferably halogen and especially bromine, with a compound of formula III

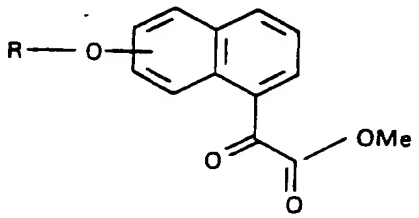
R-O-M (III)

where M is an organometallic radical or hydrogen.

When M is hydrogen, the reaction is carried out under basic conditions e.g. in the presence an alkali metal carbonate or hydroxide, and also in the presence of a metal salt catalyst, such as cuprous iodide.

The compounds of formula II are known, e.g. EP 538097, or can be prepared in known manner.

b) by reacting a compound of formula IV



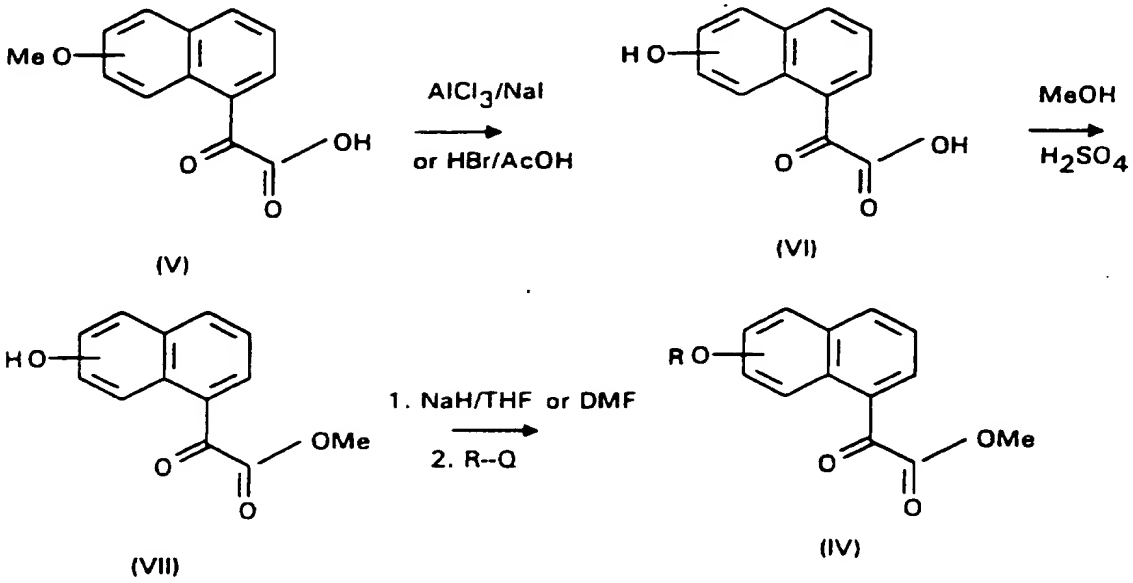
(IV)

with a phosphorus ylide derived from e.g. a phosphonium salt of formula

$Ph_3P^+CH_2OMe\ \ Hal^-$

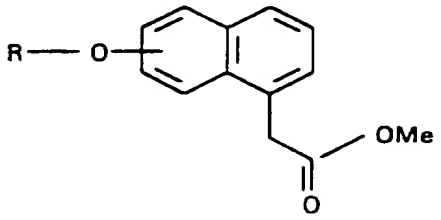
under basic conditions.

The compounds of formula IV can be prepared by the following reaction scheme.



where Q is a leaving group, e.g. a halide or a sulfonate, THF is tetrahydrofuran and DMF is dimethylformamide.

c) by reacting a compound of formula IX

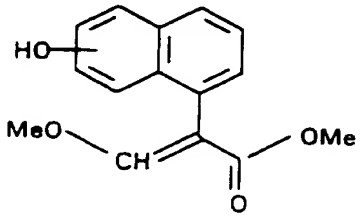


(IX)

with methyl formate under basic conditions, followed by methylation of the resulting hydroxypropenoate.

The compound of formula IX can be obtained by reducing the compounds of formula IV, in a Wolff-Kischner reduction, e.g. by using hydrazine in the presence of a base e.g. an alkali metal alkoxide.

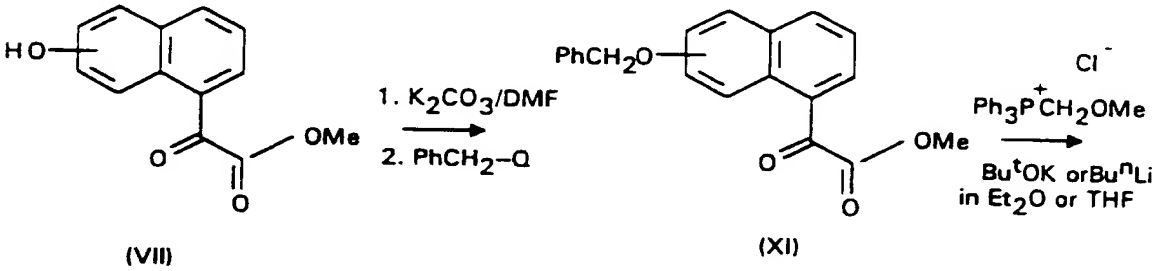
d) by reacting a compound of formula X



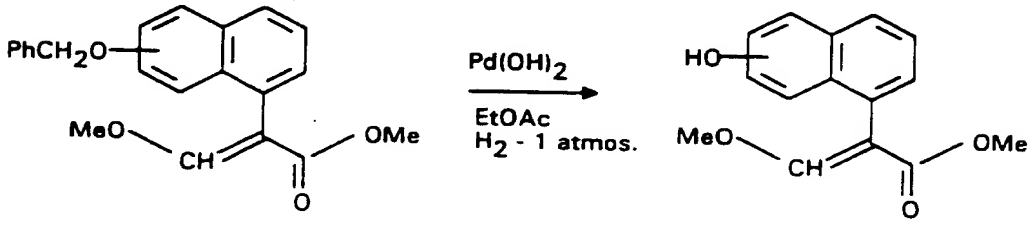
(X)

with a compound of formula R-Q where Q is a leaving group e.g. a halogen, sulfonate or sulfone under basic conditions. Compounds of formula X can be prepared from compounds of formula VII according to the following schemes.

Scheme (a) - via benzylic protection

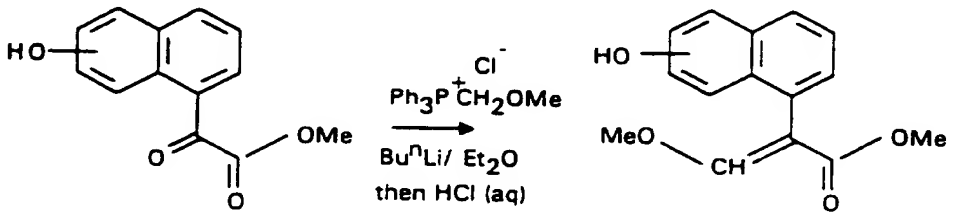


(VII) (XI)



(XII) (X)

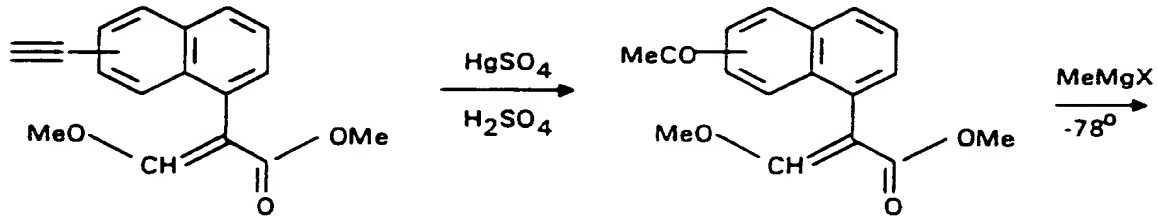
Scheme (b) - direct conversion



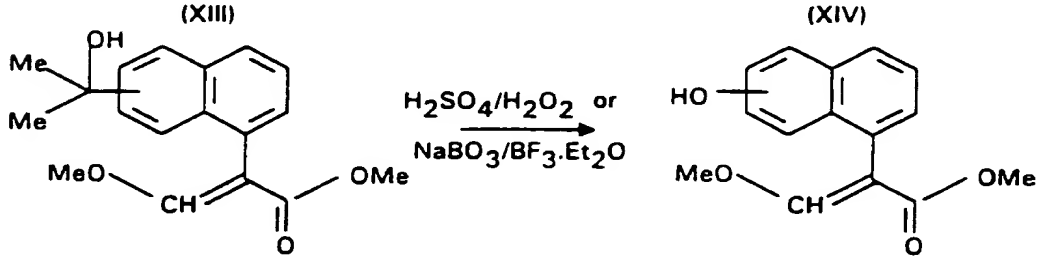
(VII) (X)

Scheme (c) - from an acetylenic precursor

Acetylenic compounds (XIII) are described in EP 566,455 (Roussel Uclaf) and may be converted to compounds (X) according to the following scheme.



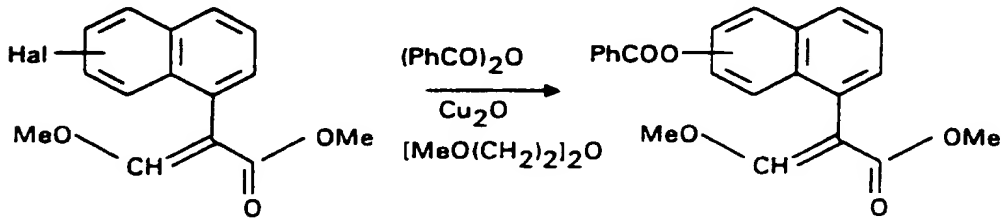
(XIII) (XIV)



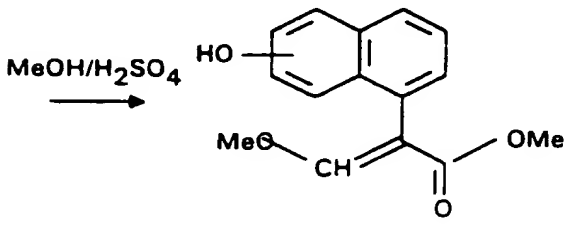
(XV) (X)

Scheme (d) - from a halide precursor

Halo compounds (XVI) are described in EP 566,455 (Roussel Uclaf) and may be converted to compounds (X) according to the following scheme.

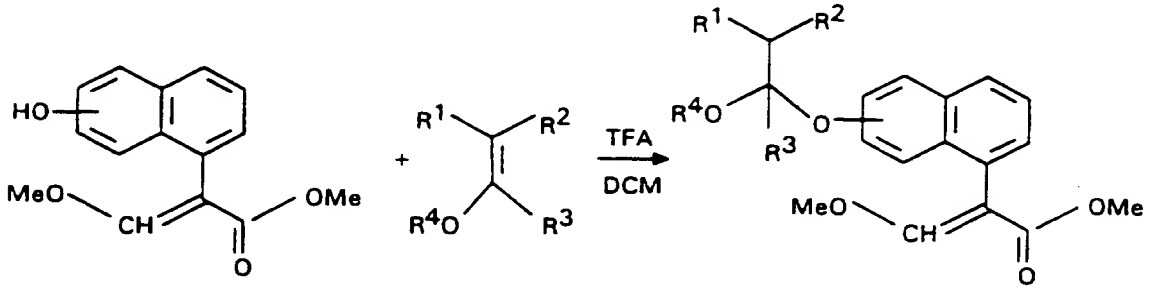


(XVI) (XVII)



(X)

e) by reacting a compound of formula X with a vinyl ether of formula XVIII in the presence of a protic or Lewis acid, e.g. trifluoroacetic acid (TFA) in e.g. a halogenated solvent., e.g. dichloromethane (DCM)



(X) (XVIII) (XIX)

where R^1, R^2 and R^3 are hydrogen or alkyl and R^4 is alkyl.

Other methods will be apparent to the chemist skilled in the art as will be the methods for preparing starting materials and intermediates. The Examples also make apparent various methods of preparing compounds of the invention as well as starting materials and intermediates.

The invention is illustrated in the following Examples. Structures of isolated novel compounds were confirmed by elemental and/or other appropriate analyses. Temperatures are in °C. DMF = dimethylformamide; THF = tetrahydrofuran

Example 1

Methyl (Z) and (E)-2-[7-(4,6-dimethoxypyrimidin-2-yloxy)-1-naphthyl]-3-methoxyacrylate

Potassium tert.-butoxide (1.0 g) was added to a suspension of methoxymethyl-triphenylphosphonium chloride (3.34 g) in dry ether (25 ml) under nitrogen. The mixture stirred for 30 minutes at room temperature. The supernatant liquid was decanted into a dropping funnel and added over 5 minutes, with stirring, to a solution of methyl 2-[7-(4,6-dimethoxypyrimidin-2-yloxy)-1-naphthyl]-2-oxoacetate (1.63 g) in dry tetrahydrofuran (25 ml). The mixture was stirred for 24 hours at room temperature, water was added and the organic layer removed, dried over magnesium sulfate and worked up to give the crude product as a mixture of (Z) and (E) isomers. The product was purified by silica gel chromatography using hexane:ethyl acetate (3:1) as eluent. Fractions containing the pure less polar component were combined and evaporated to give a yellow oil. This was dissolved in a mixture of di-isopropyl ether and hexane whereupon a white solid crystallised. Isolation gave methyl (E)-2-[7-(4,6-dimethoxypyrimidin-2-yloxy)-1-naphthyl]-3-methoxyacrylate as a white solid, m.p. 145°. (Compound 1a). Fractions containing the pure more polar component were similarly worked up to give methyl (Z)-2-[7-(4,6-dimethoxypyrimidin-2-yloxy)-1-naphthyl]-3-methoxy-acrylate, as a white solid, m.p 129-131°. (Compound 1b)

Preparation of starting materials

a) 2-(7-Hydroxy-1-naphthyl)-2-oxoacetic acid

2-(7-Methoxy-1-naphthyl)-2-oxoacetic acid (25.63 g) (prepared according to the method of Gottlieb, Kellner and Loewenthal; Synth. Comm. (1989) 2987-2997) in dry dichloromethane (800 ml) was added over 30 minutes to a stirred suspension of aluminium trichloride (59.5 g) in dry dichloromethane (500 ml). Sodium iodide (67 g) was added in one portion with stirring and the mixture was stirred at room temperature for 18 hours. It was poured into water (2 litres) containing concentrated hydrochloric

acid (300 ml) and the solid broken up. Eventually an orange solid was deposited. This was filtered and washed with water to give the desired product as an orange powder, m.p. 220-3° (dec).

b) Methyl 2-(7-hydroxy-1-naphthyl)-2-oxoacetate

2-(7-Hydroxy-1-naphthyl)-2-oxoacetic acid (2.40 g) and methanol (50 ml) containing conc. sulfuric acid (5 drops) were heated under reflux for 1 hour. The solvent was removed *in vacuo* and the residue dissolved in ethyl acetate. The solution was washed with aqueous sodium bicarbonate, dried over magnesium sulfate and worked up to give a brown solid. This was purified by silica gel chromatography using hexane:ethyl acetate (1:1) as eluent. to give the title product as a yellow solid), m.p. 126-8°.

c) Methyl 2-[7-(4,6-dimethoxypyrimidin-2-yloxy)-1-naphthyl]-2-oxoacetate

Sodium hydride (60% in mineral oil; 0.35 g) was added portionwise, with stirring to a solution of methyl 2-(7-hydroxy-1-naphthyl)-2-oxoacetate (20 g) in dry dimethylformamide (20 ml). After stirring for 10 minutes at room temperature a solution containing 4,6-dimethoxy-2-methylsulfonyl-pyrimidine (1.88 g) in dry dimethylformamide (5 ml) was added and the mixture was stirred at room temperature for 60 hours. The reaction mixture was poured into water, extracted with ethyl acetate, the extract washed with brine, dried over magnesium sulfate and worked up to give a brown oil. This was purified by silica gel chromatography using hexane:ethyl acetate (2:1) as eluent to give a brown oil which was triturated with di-isopropyl ether to give the title compound as a white solid, m.p. 99-100°.

Example 2

Methyl (E)-2-[7-(3,4-dichlorophenoxy)-1-naphthyl]-3-methoxyacrylate

A mixture of methyl (E)-2-(7-bromo-1-naphthyl)-3-methoxyacrylate (3 g), 3,4-dichlorophenol (3 g), potassium carbonate (2.4 g) and cuprous iodide (100 mg) was heated at 170° for (100 mg) was heated at 170° for 5 hours, under nitrogen. The mixture was cooled and water and dichloromethane added. The organic extract was worked up to give the title product, m.p. 128° (Compound 2)

Example 3

Methyl (E)-2-[7-propoxy-1-naphthyl]-3-methoxyacrylate

Methyl (E)-2-[7-hydroxy-1-naphthyl]-3-methoxyacrylate (1 g) in dry DMF (10 ml) was stirred at room temperature under nitrogen as sodium hydride (0.2 g of 60% in mineral oil) was added portionwise. After stirring for 15 minutes, propyl iodide (0.85 g) was added in one portion and the reaction mixture stirred a further 1 hour at room temperature. The reaction mixture was poured onto water whereupon extraction with ethyl acetate gave the crude product as a brown oil. The oil was dissolved in diisopropyl ether (5 ml) and hexane (12 ml) and decanted from a small amount of tarry material. On cooling in ice a white solid was precipitated. Isolation gave methyl (E)-2-[7-propoxy-1-naphthyl]-3-methoxyacrylate, m.p. 74-75.5° (Compound 65 - see also in table later).

Preparation of the starting material

(i) via benzylic protection

a) Methyl 2-(7-benzyloxy-1-naphthyl)-2-oxoacetate

To methyl 2-(hydroxy-1-naphthyl)-2-oxoacetate (10.35 g) in dry DMF (100 ml) was added powdered potassium carbonate (7 g), stirred for 10 minutes before adding dropwise, benzyl bromide (6 ml). After stirring for 4½ hours at room temperature, the DMF was removed *in vacuo*. The residue was quenched with water. Extraction with ethyl acetate gave the product as a yellow oil that crystallised from ether and hexane. Isolation gave the title product, m.p 82-83.5°

b) Methyl (E)-2-[7-benzyloxy-1-naphthyl]-3-methoxyacrylate

To methyl 2-[7-benzyloxy-1-naphthyl]-2-oxoacetate (1.6 g) in dry THF (40 ml) under nitrogen was slowly added an excess of the Wittig reagent generated from (methoxymethyl)triphenylphosphonium chloride (4.1 g) in dry ether and 2.5M butyl lithium in hexane (4.8 ml). When a deep red colour persisted, the addition was stopped and the reaction mixture stirred for 24 hours at room temperature. The reaction mixture was quenched with dilute hydrochloric acid and extracted with ethyl acetate. Isolation gave the product as a mixture of (E) and (Z) isomers that were separated by chromatography on silica gel using 20-35% ethyl acetate in hexane under gradient elution conditions. Isolation gave predominantly methyl (E)-2-[7-benzyloxy-1-naphthyl]-3-methoxyacrylate, m.p 122-125° (compound 36 (see

also in table later) as the major product and methyl (Z)-2-[7-benzyloxy-1-naphthyl]-3-methoxyacrylate, m.p. 122, as the minor product (compound 36a).

c) Methyl (E)-2-[7-hydroxy-1-naphthyl]-3-methoxyacrylate

To methyl (E)-2-[7-benzyloxy-1-naphthyl]-3-methoxyacrylate (5.2 g) in ethyl acetate (100 ml) was added 20% palladium hydroxide on carbon (300 mg). The mixture was hydrogenolysed at room temperature and 1 atmosphere pressure until all of the starting material was shown by TLC analysis to have reacted. Removal of the catalyst by filtration, evaporation of the solvent and trituration with 20% ethyl acetate in hexane gave methyl (E)-2-[7-hydroxy-1-naphthyl]-3-methoxyacrylate, m.p. 198-199.5°.

(ii) via direct reaction

Methyl (E and Z)-2-[7-hydroxy-1-naphthyl]-3-methoxyacrylate

49.5 g (0.144 mol) (methoxymethyl)triphenylphosphonium chloride was suspended in 400 ml dry ether. The reaction mixture was cooled to 0°, 57.6 ml (0.144 mol) n-butyllithium (2.5 m in hexane) was the added with syringe over a period of 5 minutes. The bright red suspension was allowed to come to room temperature and then stirred for 30 minutes. The formed solid was allowed to settle. The solution was transferred into another flask using a cannula. The residue was washed with 100 ml dry ether. The ether phases were combined. A solution of 11.08 g (0.048 mol) methyl 2-(7-hydroxynaphthyl)-2-oxoacetate in 100 ml dry acetonitrile was added to give a dark red solution. After stirring for 2 hours 150 ml water were added. The aqueous layer was acidified with hydrochloric acid and extracted with ethyl acetate. The organic layer was washed with aqueous sodium hydrogen carbonate, then water, dried over magnesium sulfate, some charcoal was added, the suspension filtered and the solvent evaporated to give 37.8 g of a brown oil. This was submitted to column chromatography on silica gel using ethyl acetate: light petroleum (1:10 gradually changing to 1:1). 8.7 g (70%) E ad Z isomer were obtained as 1:1 mixture.

iii) From an acetylenic precursor

Methyl (E)-2-[7-acetyl-1-naphthyl]-3-methoxyacrylate

Methyl (E)-2-[7-ethynyl-1-naphthyl]-3-methoxyacrylate was dissolved in acetone (500 ml) and added over 5 minutes with cooling to a solution containing concentrated sulfuric acid (24 ml), water (216 ml) and mercury (II) sulfate (20 g). When the addition was complete, further acetone (500 ml) and THF (15 ml) were added. The mixture was heated to 55° for 2 hours before cooling and pouring onto water. Extraction with ether and subsequent isolation gave the product as a yellow-brown solid that was further purified by column chromatography. Isolation gave the title product, m.p. 141-142.5°.

Methyl (E)-2-[7-(1-hydroxy-1-methylethyl)-1-naphthyl]-3-methoxyacrylate

Methyl (E)-2-[7-acetyl-1-naphthyl]-3-methoxyacrylate (1.0 g) was dissolved in dry ether (10 ml) and dry dichloromethane (10 ml) and cooled to -78° under an atmosphere of nitrogen. Methyl magnesium bromide (2.4 ml of a 3M solution in ether) was added directly and the reaction mixture stirred for 2 hours at -78° before warming to room temperature and then pouring onto water (100 ml) and dichloromethane (100 ml). Isolation gave the product as a yellow solid, which was used without further purification.

Methyl (E)-2-[7-hydroxy-1-naphthyl]-3-methoxyacrylate

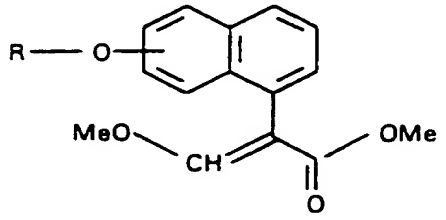
Sodium perborate tetrahydrate (308 mg) in dry THF (12.4 ml) was stirred as boron trifluoride etherate (1.72 ml) was added at 0° and the mixture stirred for 30 minutes before adding methyl (E)-2-[7-(1-hydroxy-1-methylethyl)-1-naphthyl]-3-methoxyacrylate (300 mg) in dichloromethane (7.5 ml). The mixture was then heated at 50° for 18 hours before pouring onto water and extracting the product. Isolation gave methyl (E)-2-[7-hydroxy-1-naphthyl]-3-methoxyacrylate which was identical to samples prepared via the methods previously described.

Example 4

Methyl (E)-2-[7-(2-chloro-1,1,2,2,-tetrafluoroethoxy)-1-naphthyl]-3-methoxy-acrylate

Methyl (E)-2-[7-hydroxy-1-naphthyl]-3-methoxyacrylate (12.28 g) was dissolved in dry N-methylpyrollidinone (NMP) (200 ml). Sodium hydride (60% in mineral oil; 3.8 g) was added portionwise and the solution stirred for 30 minutes at room temperature. 1,2-Dichlorotetrafluoroethane (35 ml) was condensed into a flask at -78°C and added in one portion to the reaction mixture. When all the starting material had been shown by tlc, to have reacted (3 hours), the reaction mixture was carefully poured onto ice-water and acidified with hydrochloric acid. Extraction with ethyl acetate gave the product as a dark oil that was further purified by flash column chromatography on silica gel using 5:2 hexane:ethyl acetate as eluent. Isolation and crystallisation from hexane gave the title product, m.p. 76.5-77°C. (Compound 112 - also in table later).

In a similar manner to the previous Examples, the following compounds of formula I were obtained:



(I)

Cpd	R	Position of R-O-	E/Z	m.p.(°)
3	Me	7	E	110-6
4	pyrimidin-2-yl	7	E	169-70
5	6-Cl-pyrimidin-4-yl	7	E	152.5-3.5
6	2-benzoxazolyl	7	E	165-6
7	5-CF_3-1,3,4-thiadiazol-2-yl	7	E	105-7
8	5-CF_3-1,3,4-thiadiazol-2-yl	7	Z	100.5-10
9	4,6-$(MeO)_2$-1,3,5-triazin-2-yl	7	E	142-4
10	4,6-$(MeO)_2$-1,3,5-triazin-2-yl	7	Z	82-6
11	pyrazin-2-yl	7	E	153-5
12	pyrazin-2-yl	7	Z	139-41
13	6-Cl-pyridazin-3-yl	7	E	176-8
14	6-Cl-pyridazin-3-yl	7	Z	152-4
15	pyridin-2-yl	7	E	157-98
16	3-(MeOCO)-pyridin-2-yl	7	E	144-6
17	4F-C_6H_4-	7	E	99-100
18	4Cl-C_6H_4	7	E	132
19	3Cl-C_6H_4	7	E	83
20	2Cl-C_6H_4	7	E	88
21	2-NC-C_6H_4	7	E	118
22	Ph-	7	E	86
23	3-Ph-1,2,4-thiadiazol-5-yl	7	E	184.5-7
24	quinoxalin-2-yl	7	E	215-67
25	pyrimidin-2-yl	7	Z	128.5-30
26	2-benzoxazolyl	7	Z	145-6.5

Cpd	R	Position of R-O-	E/Z	m.p.(°)
27	6-Cl-pyrimidin-4-yl	7	Z	111-1.5
28	3-Ph-1,2,4-thiadiazol-5-yl	7	Z	170.5-1.5
29	quinoxalin-2-yl	7	Z	182.5-5
30	5-NC-pyridin-2-yl	7	E	200-2
31	5-NC-pyridin-2-yl	7	Z	177-9
32	5-Cl-3-benzisoxazolyl	7	E	117-9
33	quinazolin-4-yl	7	E/Z	100-5
34	Pr^i	7	E	96-8
35	1-Ph-tetrazol-5-yl	7	E	167-9
37	5-CF_3-benzothiazol-2-yl	7	E	171-7
38	5-CF_3-benzothiazol-2-yl	7	Z	167-72
39	3-methylbut-2-en-1-yl	7	E	90
40	4-MeO-benzyl	7	E	Oil
41	4-MeO-benzyl	7	Z	Oil
42	3-(2-CF_3-C_6H_4)-1,2,4-thiadiazol-5-yl	7	E	40
43	6-Cl-quinazolin-4-yl	7	E	114
44	3-(4-Cl-C_6H_4)-1,2,4-oxadiazol-5-yl	7	E	169
45	FCH_2CH_2-	7	E	116-8
46	3,4-$(MeO)_2$-C_6H_3	6	E	123-4
47	Bu^t-	7	E	74-120
48	Ph-	6	E	143-4
49	prop-2-en-1-yl	7	E	60-6
50	prop-2-en-1-yl-	7	Z	102-5
51	4-PhO-pyrimidin-2-yl	7	E	172-5
52	benzisoxazol-3-yl	7	E	48-122
53	3-CN-pyrazin-2-yl	7	E	158-165
54	6-MeO-pyrimidin-4-yl	7	E	121-3
55	3-CF_3-pyridin-2-yl	7	E	116-8
56	prop-2-yn-1-yl	7	E	124-8
57	$NC.CH_2$-	7	E	105-6
58	5-bromopyrimidin-4-yl	7	E	144-5

Cpd	R	Position of R-O-	E/Z	m.p.(°)
59	$(CH_3)_2CHCH_2$-	7	E	99-102
60	cyclopropylmethyl-	7	E	80-2
61	5-(4-Cl-C_6H_4)-1,2,4-oxadiazol-2-yl	7	E	233-5
62	difluoromethyl	7	E	92-3
63	5-Cl-6-Et-pyrimidin-4-yl	7	E	155-7
64	2-Me-prop-2-en-1-yl	7	E	93.5-4.5
65	Pr^n	7	E	74-5.5
66	6-F-quinazolin-4-yl	7	E	154-7
67	7-Cl-quinazolin-4-yl	7	E	165-8
68	sec-butyl	7	E	77-8
69	1-ethylpropyl	7	E	94.5-5.5
70	1-methylbutyl	7	E	71-2
71	α-methylbenzyl	7	E	156-7
72	Et	7	E	99-100
73	Bu^n	7	E	68-9
74	α-methyl-3-CF_3-benzyl	7	E	119-120
75	4-Cl-benzyl	7	E	149-5-
76	2-methylbenzyl	7	E	104-5
77	5-(4-Cl-phenyl)-4,5-dihydroisoxazol-3-yl	7	E	152-3
78	$EtNHCOCH_2$	7	E	155-6.5
79	cyclopentyl	7	E	Oil
80	1-methylpentyl	7	E	Oil
81	prop-2-ynyl	7	E	145-6
82	3-CN-pyridin-2-yl	7	E	180-1
83	6,7-Cl_2-quinazolin-4-yl	7	E	211-3
84	2-Me-quinazolin-4-yl	7	E	220-1
85	3-isopropyl-1,2,4-thiadiazol-5-yl	7	E	97-8
86	cyclohex-2-en-1-yl	7	E	107-8
87	8-Cl-quinazolin-4-yl	7	E	185-7
88	1-ethoxyethyl	7	E	Oil
89	cyclohexyl	7	E	109-11

Cpd	R	Position of R-O-	E/Z	m.p.(°)
90	6-(2-F-C_6H_4O)-pyrimidin-4-yl	7	E	Glass
91	benzo-1,2,3-triazin-4-yl	7	E	137-9
92	4-cyclopropyl-6-Me-pyrimidin-2-yl	7	E	131-3
93	6-Ph-pyrimidin-4-yl	7	E	146-8
94	quinolin-2-yl	7	E	174-6
95	6-(2-CN-C_6H_4O)-pyrimidin-4-yl	7	E	63-7
96	$MeOCH_2CH_2$-	7	E	110-1
97	(2,4,6-Cl_3-C_6H_3)-OCH_2CH_2-	7	E	114-5
98	$PhOCH_2CH_2$-	7	E	99-101
99	PhCOCH(Me)-	7	E	Oil
100	$MeOCOCF_2$-	7	E	Oil
101	5-(2,4-Cl_2-C_6H_3)-pyrimidin-4-yl	7	E	Gum
102	5-(4-Cl-C_6H_4)-pyrimidin-4-yl	7	E	Gum
103	6-MeS-quinazolin-4-yl	7	E	178-80
104	$EtOCH_2CH_2$	7	E	Oil
105	5-(4-Br-C_6H_4)-pyrimidin-4-yl	7	E	124-6
106	6-Me-quinazolin-4-yl	7	E	150.5-2.5
107	5-(4-Me-C_6H_4)-pyrimidin-4-yl	7	E	133-5
108	Cl CF_2 CClF-	7	E	83.5-7
109	$PhO(CH_2)_3$-	7	E	100-1.5
110	$PhO(CH_2)_4$-	7	E	78.5-80
111	$BrCF_2$-	7	E	58-61
112	$ClCF_2$-CF_2-	7	E	76-7.5
113	Cl_2FC-CFCl-	7	E	99-103
114	ClF_2C-CFCl-	7	E	Oil
115	benzyl	7	Z	122
116	HCF_2-CF_2-	7	E	79-80
117	$ClCF_2$-CF_2-	5	E	
118	$ClCF_2$-CF_2-	6	E	
119	$ClCF_2$-CF_2-	8	E	
120	$ClCF_2$-CFCl-	6	E	

Cpd	R	Position of R-C-	E/Z	m.p.(°)
121	CCl_3-CCl_2-	7	E	
122	$F_2C=CF$-	7	E	
123	$F_2C=CCl$-	7	E	
124	$Me_2C=CF$-	7	E	
125	$MeOCF_2$-CF_2-	7	E	
126	$NCCF_2$-CF2-	7	E	
127	$PhOCF_2$-CF2-	7	E	
128	2-pyridylOCF_2-CF_2-	7	E	
129	3-pyridylOCF_2-CF_2-	7	E	
130	4-pyridylOCF_2-CF_2-	7	E	
131	2-pyrimidinyl-OCF_2-CF_2-	7	E	
132	4-pyrimidinyl-OCF_2-CF_2-	7	E	
133	$(CF_3)_2CF$-	7	E	
134	CF_3CF_2-	7	E	
135	$CF_3(CF_2)_2$-	7	E	
138	$CF_3(CF_2)_3$-	7	E	
139	$CF_3(CF_2)_4$-	7	E	
140	CH_3CF_2-	7	E	
141	$F_2C=CF$-CF_2-	7	E	
141	$HC\equiv C$-CF_2-	7	E	
142	cyclopropyl-CF_2-	7	E	
143	BrF_2C-CF_2-	7	E	
144	CF_3-CFH-CF_2-	7	E	
145	$PhO(CH_2)_2$	6	E	
146	2-CN-$C_6H_4O(CH_2)_2$	7	E	
147	2-MeO-$C_6H_4O(CH_2)_2$	7	E	
148	2,3-methylenedioxy-$C_6H_3O(CH_2)_2$	7	E	
149	3-pyridyl$O(CH_2)_2$	7	E	
150	2-pyridyl$O(CH_2)_2$	7	E	
151	3-NC-2-pyridyl$O(CH_2)_2$	7	E	
152	$C_6H_5OCH_2$	7	E	

Cpd	R	Position of R-O-	E/Z	m.p.(°)
153	2-Me-6-C_6H_5-pyrimidin-4-yl	7	E	
151	6-(2-NC-C_6H_4)-pyrimidin-4-yl	7	E	
151	6-(2-pyridyl)pyrimidin-4-yl	7	E	
151	6-(3-pyridyl)pyrimidin-4-yl	7	E	
151	6-(4-pyridyl)pyrimidin-4-yl	7	E	
151	5-(2-pyridyl)pyrimidin-4-yl	7	E	

Those compounds in the above table which do not have discrete melting points have the following characteristic nmr data

Compound 40	^{1}HNMR($CDCl_3$) 3.68 (3H, s, OMe), 3.82 (3H, s, OMe), 3.86 (3H, s, OMe), 5.06 (2H, s, CH_2), 6.95 (2H, d, 9Hz, aryl), 7.08-7.44 (6H, m, aryl), 7.78 (3H, m, aryl + -OCH=C)
Compound 41	^{1}HNMR($CDCl_3$) 3.64 (3H, s, OMe), 3.85 (3H, s, OMe), 3.98 (3H, s, OMe), 5.09 (2H, s, CH_2), 6.68 (1H, s, -OCH=C), 6.96 (2H, d, 9Hz, aryl), 7.20-7.47 (6H, m, aryl), 7.80 (2H, m, aryl)
Compound 47	^{1}HNMR($CDCl_3$) 1.38 (9H, s, t-Bu), 3.66 (3H, s, OMe), 3.80 (3H, s, OMe), 7.18 (dd, 1H, 9Hz, 2Hz, aryl), 7.31 (2H, m, aryl), 7.42 (1H, tr, 7Hz, aryl), 7.78 (3H, m, aryl + -OCH=C)
Compound 52	^{1}HNMR($CDCl_3$) 3.68 (3H, s, OMe), 3.83 (3H, s, OMe), 6.97-7.60 (9H, m, aryl), 7.79 (1H, m, aryl), 7.80 (1H, s, -OCH=C), 7.87 (1H, d(broad), 9Hz, aryl), 7.98 (1H, d, 9Hz, aryl)
Compound 79	^{1}HNMR ($CDCl_3$) 1.65 (2H, M), 1.9 (6H, M), 3.7 (3H, s, OCH_3), 3.85 (3H, s, OCH_3) 4.85 (1H, m, CH), 7.0-7.8 (7H, m, aromatics + CH)

Compound 80	^{1}HNMR ($CDCl_3$) 0.9 (3H, t, CH_3), 1.3 (3H, d, CH_3),1.6 (6H, m, CH_2?) 3.7 (3H, s, CH_3O), 3.8 (3H, s, CH_3O), 4.45 (1H, MCHO), 7.05-7.8 (7H, m aromatics + CH)
Compound 88	^{1}HNMR ($CDCl_3$) 1.22 (3H, t, CH_3CH_2), 1.56 (3H, d, CH_3CH), 3.56 (2H, dq, CH_3CH_2), 3.70 (3H, s, CH_3O), 3.82 (3H, s, CH_3O), 5.52 (1H, g, $CHCH_3$), 7.2-7.9 (6H, m, aromatics, 7.82 (1H, s, CH)
Compound 90	^{1}HNMR ($CDCl_3$) 3.68 (3H, s, CH_3O), 3.82 (3H, s, CH_3O), 6.4 (1H, s, pyrimidine CH), 7.14-7.58 (8H, aromatics / 7.75 (1H, s, CH), 7.88 (1H, d, aromatics), 7.95 (1H, d, aromatics) 8.55 (1H,s,pyrimidine CH), 8.76 (1H,s,pyrimidine CH).
Compound 99	^{1}HNMR ($CDCl_3$) 1.74 (3H, d, CH_3), 3.5-3.82 (6H, br-restricted rotation, 2xCH_3O), 5.64 (H, s, CH CH_3), 7.75 (1H, s, CH), 6.92-8.12 (11H, m, aromatics)
Compound 100	^{1}HNMR ($CDCl_3$) 3.72-3.96 (9H, br-m, 3xCH_2O-restricted rotation), 7.02-7.90 (7H, m, aromatics 8 CH)
Compound 101	^{1}HNMR ($CDCl_3$) 3.64 (3H, s, CH_3O), 3.90 (3H, s, CHO_3), 7.25-76 (7H, m, aromatics), 7.72 (1H, s, CH=), 7.84 (1H, d, aromatics), 7.95 (1H, d, aromatics), 8.55 (1H, s, pyrimidine CH), 8.76 (1H, s, pyrimidine CH)

Compound 104

^{1}HNMR ($CDCl_3$)

1.26 (3H, t, $\underline{CH_3}CH_2$), 3.65(2H,q,$CH_3\underline{CH_2}$),

3.66 (3H, s, CH_3O), 3.84 (3H, s, CH_3O),

3.86 (2H, t, CH_2), 4.20 (2H, t, CH_2),

7.0-7.9 (6H, m, aromatics) 7.82 (1H, s, $\underline{CH}$)

Compound 114

^{1}HNMR ($CDCl_3$)

3.7 (3H, s, CH_3O), 3.84 (3H, s, CH_3O), 5.98 (1H, t, $\underline{CH}Cl_2$), 7.82 (1H, s, $\underline{CH}$=) 7.34-7.90 (6H, m, aromatics)

19 F NMR ($CDCl_3$)

-80.09 (2F, d, $CH\text{-}CF_2Cl$)

Test Examples

1 Fungicidal Activity

Compounds are assessed for activity against one or more of the following:

Phytophthora infestans: late tomato blight (PI)

Plasmopara viticola: vine downy mildew (PV)

Erysiphe graminis: barley powdery mildew (EG)

Pyricularia oryzae: rice blast (PO)

Pellicularia sasakii: rice sheath blight (PS)

Botrytis cinerea: grey mould (BC)

Venturia inaequalis: apple scab (VI)

Leptosphaeria nodorum: glume blotch (LN)

Aqueous solutions or dispersions of the compounds at the desired concentration, including a wetting agent, were applied by spray or by drenching the stem base of the test plants, as appropriate. Plants or plant parts were then inoculated with appropriate test pathogens and kept under controlled environment conditions suitable for maintaining plant growth and development of the disease. After an appropriate time, the degree of infection of the affected part of the plant was visually estimated. Compounds were considered active if they gave greater than 50% control of the disease at a concentration of 500 ppm (w/v) or less.

Activities are shown in the following table (+ = active against this species)

Cpd	PI	PV	EG	PO	PS	BC	VI	LN
1a		+		+			+	
1b			+			+		
2		+	+					
3		+	+	+		+	+	
4	+	+	+			+	+	
5			+	+		+	+	+
9			+			+	+	
10			+				+	
11		+	+			+		
12		+	+				+	
13		+	+				+	
14							+	
15	+	+	+			+		

Cpd	PI	PV	EG	PO	PS	BC	VI	LN
16	+		+				+	
17	+	+	+	+	+		+	
18	+	+	+				+	
19		+	+				+	
20		+						
21		+					+	
23	+	+	+					+
24				+	+		+	
25		+					+	
26				+			+	
27				+			+	
28		+	+				+	+
30			+			+	+	
31			+			+		
32	+	+	+	+			+	+
33	+	+	+	+		+	+	+
34	+	+	+	+			+	
35	+	+	+				+	+
36		+	+	+				
37				+			+	+
38			+					+
39	+	+				+	+	
40	+	+	+	+	+	+	+	
41	+	+	+			+		
42			+		+	+	+	
43	+	+	+	+	+	+		+
44							+	
45	+	+	+				+	
46	+						+	
47			+		+		+	
49	+	+	+	+	+		+	
50	+	+	+	+	+		+	

Cpd	PI	PV	EG	PO	PS	BC	VI	LN
51	+	+	+	+	+			
52	+			+		+	+	+
53	+							
54	+		+	+	+		+	
55	+	+	+	+	+	+	+	
56	+	+	+		+	+	+	
57	+			+		+		
58	+		+	+	+	+	+	+
59	+				+			
60	+		+		+		+	+
61		+				+		
62			+	+		+	+	+
63			+	+	+	+		+
64	+		+	+			+	
65				+	+		+	+
66	+		+	+	+		+	
67	+		+	+	+		+	+
68	+	+	+		+		+	
69	+	+	+		+		+	
70			+		+		+	
71			+					
72			+				+	+
73			+	+	+		+	+
74			+		+		+	+
75								+
76			+		+		+	
77			+		+			+
78						+		
79	+	+	+				+	
80		+	+		+	+	+	+
81	+	+	+		+			
82		+	+			+		

Cpd	PI	PV	EG	PO	PS	BC	VI	LN
83		+			+			
84		+		+		+	+	
85		+	+	+	+			
86				+			+	
87			+	+	+	+	+	+
88			+					
89		+			+		+	
90		+	+		+			+
91		+		+				
92			+					
93		+	+	+	+		+	+
94		+	+	+	+			
95			+	+				
96					+			
97			+	+				+
98			+	+	+			+
99				+				
100				+				
101			+	+	+			+
102			+	+	+			+
103				+	+			
104		+						
105		+	+		+	+		+
106			+	+	+			+
107			+	+	+			+
108		+		+	+		+	+
109		+	+		+		+	+
110		+	+		+	+	+	+
111		+	+	+	+		+	+
112		+	+		+		+	+
113		+	+		+		+	
114		+	+	+	+		+	+

Cpd	PI	PV	EG	PO	PS	BC	VI	LN
116		+	+	+	+		+	+

2 Insecticidal/acaricidal

- ***Aphis craccivora***

Bean plants are treated by dipping the leaves in an aqueous acetone solution of active ingredient (50% acetone, 50% water) then dried under a ventilated hood. The leaves are then infested with 20 adult *Aphis craccivora* females per leaf and kept at 22° under a intense light conditions. Mortality checks are carried out after 48 hours. Compounds were considered active if they gave greater than 75% mortality of the insects at a concentration of 300 ppm(W/v) or less. Activities are shown in the following table

- ***Tetranychus urticae***

Haricot bean plants are used comprising 2 leaves infested with 30 *Tetranychus urticae* females per leaf and put under a ventilated hood under a luminous ceiling with constant illumination. The plants are treated with a 4 ml of an aqueous acetone solution of active ingredient per plant. The leaves are left to dry for 30 minutes. Mortality checks are carried out after 72 hours. Compounds were considered active if they gave greater than 75% mortality of the insects at a concentration of 300 ppm(W/v) or less. Activities are shown in the following table

- ***Spodoptera littoralis***

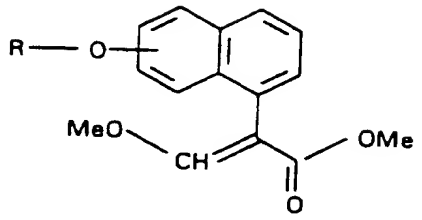
Stage L1 larvea of *Spodoptera littoralis* are added to filter paper impregnated woth aqueos acetone solution of active ingredient (50% acetone, 50% water) then dried maintained in Petri dishes. The dishes are left at 22° in 50% relative humidity conditions The number of dead larvae in counted after 7 days. Compounds were considered active if they gave greater than 75% mortality of the insects at a concentration of 300 ppm(W/v) or less. Activities are shown in the following table

+ = active against this species

Compounds	*Aphis craccivora*	*Tetranychus urt.*	*Spodoptera lit.*
3		+	+
19		+	
62	+	+	
64	+	+	
73		+	
65		+	
108	+	+	+
111	+	+	
112	+	+	+
113	+	+	+
114	+	+	+

CLAIMS

1) A compound of formula I



(I)

wherein

R is alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, phenyl or heterocyclyl, each of which is optionally substituted, or is hydrogen, and acid addition salts of any compounds which are basic and basic addition salts of any compounds which are acidic.

2) The E isomer of the compound of claim 1.

3) A compound according to claim 2 wherein the RO- group is attached to the naphthalene ring in the 7-position.

4) A compound according to claim 3, wherein R is an optionally substituted C_1-C_6 linear or branched chain alkyl group.

5) A compound according to claim 4, wherein R is optionally substituted by one or more halogen atoms.

6) A compound according to claim 5, wherein R is optionally substituted by one or more fluorine and/or chlorine and/or bromine atoms.

7) A compound according to claim 6 wherein R is CF_2H, CF_2Br, CF_2CF_2Cl, $CFClCF_2Cl$, CF_2CF_2H or CF_2CHCl_2.

8) A compound according to claim 4 wherein R is alkyl, optionally substituted by one or more alkoxy, aryloxy, heteroaryloxy or heterocyclyoxy groups, (all of which may be optionally substituted).

9) A compound according to claim 8 wherein R is Y-O-$(CH_2)_n$-, where Y is optionally substituted aryl, heteroaryl, heterocyclyl and heteroaryl, and n = 1-4.

10) A compound according to claim 9 wherein n is 2

11) A compound according to claim 3 wherein R is optionally substituted heteroaryl.

12) A compound according to claim 11 wherein R is optionally substituted pyrimidinyl, 1,2,4-thiadiazolyl, quinazolinyl or pyridyl.

13. Pesticidal, especially fungicidal, compositions which comprise a compound as claimed in any one of the preceding claims in admixture with an agriculturally acceptable diluent or carrier.

14. A method of combating pests, especially phytopathogenic fungi, at a locus infested or liable to be infested therewith, which comprises applying to the locus a compound as claimed in any one of claims 1 to 12.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/GB 96/00658

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C69/734 A01N37/14 A01N37/06 A01N31/14 A01N31/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 267 734 (ICI PLC) 18 May 1988 see the whole document ---	1-10
A	EP,A,0 178 826 (ICI PLC) 23 April 1986 see the whole document ---	1-10
A	EP,A,0 538 097 (ROUSSEL UCLAF) 21 April 1993 see the whole document ---	1-10
A	WO,A,94 23576 (ROUSSEL UCLAF ;BRAUN PETER (DE); SACHSE BURKHARD (DE)) 27 October 1994 see the whole document ---	1-10
A	EP,A,0 566 455 (ROUSSEL UCLAF) 20 October 1993 see the whole document ---	1-10

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 June 1996	05.07.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Slootweg, A

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INTERNATIONAL SEARCH REPORT

Inter[illegible]cation No
PCT/GB 96/00658

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

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